Clase 34 29 Sep 2015

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Obtención de a y b de Van der Waals (en el punto crítico)

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2}$$

Sabiendo que en el punto crítico:

$$\left(\frac{\partial P_c}{\partial \bar{V}_c}\right)_{p.c.} = 0 \qquad \left(\frac{\partial^2 P_c}{\partial \bar{V}_c^2}\right)_{p.c.} = 0 \quad ✓$$

$$P_c = \frac{RT_c}{(\bar{V}_c - b)} - \frac{a}{\bar{V}_c^2} \quad \cdots\cdots \quad (1)$$

$$\left(\frac{\partial P_c}{\partial \bar{V}_c}\right)_{p.c.} = \frac{-RT_c}{(\bar{V}_c - b)^2} + \frac{2\bar{V}_c a}{(\bar{V}_c)^4}$$

$$= \frac{-RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{(\bar{V}_c)^3} = 0 \quad \cdots\cdots \quad (2)$$

$$\left(\frac{\partial^2 P_c}{\partial \bar{V}_c^2}\right)_{p.c.} = \frac{2(\bar{V}_c - b)RT_c}{(\bar{V}_c - b)^4} - \frac{6a\bar{V}_c^2}{(\bar{V}_c)^6} = \frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

$$(3)$$

Primero se obtiene b de ② y ③

$$\left[\frac{-RT_c}{(\bar{V}_c-b)^2}+\frac{2a}{(\bar{V}_c)^3}=0\right]\frac{3}{\bar{V}_c}$$

$$\frac{2RT_c}{(\bar{V}_c-b)^3}-\frac{6a}{\bar{V}_c^4}=0$$

$$-\frac{3RT_c}{(\bar{V}_c-b)^2\bar{V}_c}+\frac{6a}{(\bar{V}_c)^4}=0$$

$$\frac{2RT_c}{(\bar{V}_c-b)^3}-\frac{6a}{(\bar{V}_c)^4}=0$$

arreglando

$$-\frac{3RT_c}{(\bar{V}_c-b)^2\bar{V}_c}+\frac{2RT_c}{(\bar{V}_c-b)^3}=0$$

$$-\frac{3R\cancel{T_c}}{\cancel{(\bar{V}_c-b)^2}\,\bar{V}_c}=-\frac{2\cancel{R}T_c}{(\bar{V}_c-b)^{\cancel{3}}}$$

$$3(\bar{V}_c-b)=2\bar{V}_c$$

$$3\bar{V}_c-3b=2\bar{V}_c$$

$$\bar{V}_c=3b$$

$$\boxed{b=\frac{1}{3}\bar{V}_c}=\boxed{\frac{L}{mol}}$$

para obtener a se utiliza un sistema de 3 ecuaciones 1 - 3

$$\left[P_c - \frac{RT_c}{(\bar{V}_c - b)} + \frac{a}{\bar{V}_c^{2}} = 0\right] \frac{3}{(\bar{V}_c - b)^2}$$

$$\left[- \frac{RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{\bar{V}_c^{3}} = 0\right] - \frac{1}{(V_c - b)}$$

$$\frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^{4}} = 0$$

obteniendose

$$\frac{3P_c}{(\bar{V}_c - b)^2} - \frac{3RT_c}{(\bar{V}_c - b)^3} + \frac{3a}{\bar{V}_c^2(\bar{V}_c - b)^2} = 0$$

$$\frac{RT_c}{(\bar{V}_c - b)^3} - \frac{2a}{\bar{V}_c^3(\bar{V}_c - b)} = 0$$

$$\frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

$$\frac{3P_c}{(\bar{V}_c - b)^2} + \frac{3a}{\bar{V}_c^2(\bar{V}_c - b)^2} - \frac{2a}{\bar{V}_c^3(\bar{V}_c - b)} - \frac{6a}{\bar{V}_c^4} = 0$$

$$\frac{3P_c}{(\bar{V}_c-b)^2}+\boxed{\frac{3a}{\bar{V}_c^2(\bar{V}_c-b)^2}-\frac{2a}{\bar{V}_c^3(\bar{V}_c-b)}-\frac{6a}{\bar{V}_c^4}}=0$$

Tomando solo esta parte y si $b=\tfrac{1}{3}\bar{V}_c$

$$\frac{3a}{(\bar{V}_c-\tfrac{1}{3}\bar{V}_c)^2\,\bar{V}_c^2}-\frac{2a}{(\bar{V}_c-\tfrac{1}{3}\bar{V}_c)\,\bar{V}_c^3}-\frac{6a}{\bar{V}_c^4}$$

$$\frac{3a}{(\tfrac{2}{3}\bar{V}_c)^2\,\bar{V}_c^2}-\frac{2a}{(\tfrac{2}{3}\bar{V}_c)(\bar{V}_c^3)}-\frac{6a}{\bar{V}_c^4}$$

$$\frac{3a}{\tfrac{4}{9}\bar{V}_c^4}-\frac{2a}{\tfrac{2}{3}\bar{V}_c^4}-\frac{6a}{\bar{V}_c^4}$$

$$\frac{3a}{4/9\sqrt{c^4}} - \frac{2a}{2/3\sqrt{c^4}} - \frac{6a}{\sqrt{c^4}}$$

$$\frac{3a}{4/9\sqrt{c^4}} - \frac{2a}{6/9\sqrt{c^4}} - \frac{6a}{9/9\sqrt{c^4}}$$

$$\frac{27a}{4\sqrt{c^4}} - \frac{18a}{6\sqrt{c^4}} - \frac{54a}{9\sqrt{c^4}} =$$

$$= \frac{9(27)a - 6(18)a - 4(54)a}{36\sqrt{c^4}} = -\frac{81}{36}a = \boxed{-\frac{9}{4\sqrt{c^4}}a}$$

por lo tanto retomando

$$\frac{3P_c}{(\bar{V}_c - b)^2} - \frac{9a}{4\bar{V}_c^4} = 0$$

$$\frac{3P_c}{(\bar{V}_c - 1/3\bar{V}_c)^2} = \frac{9a}{4\bar{V}_c^4}$$

$$\frac{3P_c}{(2/3\bar{V}_c)^2} = \frac{9a}{4\bar{V}_c^4}$$

$$\frac{3P_c}{\cancel{4/9}\,\cancel{\bar{V}_c^2}} = \frac{\cancel{9}a}{\cancel{4}\bar{V}_c^{\cancel{4}\,2}} \rightarrow 3P_c = \frac{a}{\bar{V}_c^2}$$

✓

$$a = 3P_c\bar{V}_c^2 = \frac{atm\,L^2}{mol^2}$$

Obtención de a ecuación original

$$p_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2} \qquad \text{sí} \quad R = \frac{8}{3}\, \frac{p_c \bar{V}_c}{T_c}$$

despejando a

$$a = \left(-p_c + \frac{RT_c}{\bar{V}_c - b}\right)\bar{V}_c^2$$

$$a = -\bar{V}_c^2 p_c + \frac{R\,T_c \bar{V}_c^2}{2/3\,\bar{V}_c} = -\bar{V}_c^2 p_c + \frac{\frac{8}{3}\,\frac{p_c \bar{V}_c}{\cancel{T_c}}\,\bar{V}_c^2\,\cancel{T_c}}{2/3\,\cancel{\bar{V}_c}}$$

por lo tanto, se obtiene:

$$a = -\rho c \bar{V}_c^2 + \frac{24}{6}\rho c \bar{V}_c^2$$

$$a = -\frac{6}{6}\rho c \bar{V}_c^2 + \frac{24}{6}\rho c \bar{V}_c^2$$

$$a = \frac{18}{6}\rho c \bar{V}_c^2 = 3\rho c \bar{V}_c^2$$

Resultado semejante

En relación ala ecuación de Van der Waals las constantes a, b, R

Se obtienen con otras ecuaciones comparadas alas obtenidas

obtenidas

$$a = 3 P_c \bar{V}_c^2$$

$$b = \frac{1}{3} \bar{V}_c^2$$

Independientes de R

$$R = \frac{8}{3} \frac{P_c \bar{V}_c}{T_c}$$

otras ecuaciones

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} = \left(\frac{atm\,L}{mol\,\cancel{K}}\right)^{\cancel{2}} \frac{(\cancel{K})^{\cancel{2}}}{(\cancel{atm})} = \frac{atm\,L^2}{mol^2}$$

$$b = \frac{R\,T_c}{8\,P_c} = \left(\frac{\cancel{atm}\,L}{mol\,\cancel{K}}\right)\left(\frac{\cancel{K}}{\cancel{atm}}\right) = \frac{L}{mol}$$

Independientes de $\bar{V}_c$

$$R = 0.082 \frac{atm\,L}{mol\,K}$$

Obtención de b

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2}$$

$$a = 3P_c(V_c)^2$$

$$\bar{V}_c = 3b$$

$$P_c = \frac{RT_c}{3b - b} - \frac{3P_c(\bar{V}_c)^2}{\bar{V}_c^2}$$

$$P_c = \frac{RT_c}{2b} - 3P_c \qquad 4P_c = \frac{RT_c}{2b}$$

$$\boxed{b = \frac{RT_c}{8P_c}} = \frac{(\cancel{at}m\,L/mol\,\cancel{K})(\cancel{K})}{8\,(\cancel{at}m)} = \frac{L}{mol}$$

obtención de a

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2} \qquad P_c = \frac{RT_c}{3b - b} - \frac{a}{(3b)^2}$$

$$P_c = \frac{RT_c}{2b} - \frac{a}{(3b)^2} = \frac{9b^2 RT_c - 2ab}{18b^3}$$

$$18b^3 P_c = 9b^2 RT_c - 2ab$$

$$\frac{-18b^3 P_c + 9b^2 RT_c}{2b} = a \qquad -9b^2 P_c + \frac{9}{2} b RT_c = a$$

$$-9\left(\frac{RT_c}{8P_c}\right)^2 P_c + \frac{9}{2}\left(\frac{RT_c}{8P_c}\right) RT_c = a$$

$$-\frac{9}{64}\,\frac{R^2T_c^2\,\cancel{P_c}}{P_c^{\cancel{2}}} + \frac{9}{16}\,\frac{R^2T_c^2}{P_c} = a$$

$$-\frac{9}{64}\,\frac{R^2T_c^2}{P_c} + \frac{9}{16}\,\frac{R^2T_c^2}{P_c} = a$$

$$-\frac{9}{64}\,\frac{R^2T_c^2}{P_c} + \frac{36}{64}\,\frac{R^2T_c^2}{P_c} = a$$

$$\boxed{\frac{27}{64}\,\frac{R^2T_c^2}{P_c} = a} \qquad \frac{27}{64}\,\frac{(\text{atm}\,L/\text{mol}\,\cancel{K})^{\cancel{2}}\,(\cancel{K})^2}{\cancel{\text{atm}}} = \frac{\text{atm}\,L^2}{\text{mol}^2}$$

Ejercicio Calcular a y b de Van der Waals para el H_2

propiedades críticas

$T_c = 33.3\ K \qquad p_c = 12.8\ atm \qquad \rho_c = 0.031\ g/cm^3$

a y b independientes de $\bar{V}_c$

$$a = \frac{27}{64}\frac{R^2 T_c^2}{p_c} = \frac{27}{64}\frac{(0.082\ atm\ L/mol\ K)^2 (33.3\ K)^2}{12.8\ atm} = \frac{0.2457\ atm\ L^2}{mol^2}$$

el cual convertido a: $\frac{atm\,cm^6}{mol^2}$

$$\left(0.2457\,\frac{atm\,L^2}{mol^2}\right)\left(\frac{1\times10^3\,cm^3}{1\,L}\right)^2 = \left(0.2457\,\frac{atm\,\cancel{L^2}}{mol^2}\right)\left(\frac{1\times10^6\,cm^6}{\cancel{L^2}}\right)$$

$$a = 24.57\times10^4\,\frac{atm\,cm^3}{mol^2}$$

calculo de b

$$b = \frac{RTc}{8\,pc} = \frac{(0.082\,atm\,L/mol\,K)(33.3\,K)}{8\,(12.8\,atm)} = 0.02667\,L/mol$$

$$b = \left(\frac{0.02667\ L}{mol}\right)\left(\frac{10^3\ cm^3}{1\ L}\right) = \frac{26.67\ cm^3}{mol}$$

Tarea obtener a y b dependiente de $\bar{V}_c$

en tablas $a = 24.56 \times 10^4 \dfrac{atm\ cm^6}{mol^2}$

$b = 26.67 \dfrac{cm^3}{mol}$

esto quiere decir que el valor de tabla se calcula con a y b independiente de $\bar{V}_c$